

# Molecular Mechanics Studies of Acyl Halides: II. Vibrational Spectra

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**ABSTRACT:** A newly developed acyl halide molecular mechanics (MM3) force field can accurately calculate molecular geometry, usually to within experimental error. The new force field can also calculate vibrational frequencies. The acyl halides studied were formyl halides, acetyl halides, propionyl halides, *n*-butyryl halides, 2-methylpropionyl halides, and 2,2-dimethylpropionyl halides. The rms deviation for vibrational frequencies was 28 cm<sup>-1</sup>. © 1998 John Wiley & Sons, Inc. J Comput Chem 19: 1387–1401, 1998

**Keywords:** acyl halides; MM3; *ab initio* calculations; IR

## Introduction

A newly derived MM3 force field is able to calculate molecular structures and vibrational frequencies for acyl halides. The molecular geometry and energetics have been described.<sup>1</sup> In the present work, for the smaller carbon acyl halides, RCOX, where R is H, CH<sub>3</sub>, or CH<sub>3</sub>CH<sub>2</sub> and X is F, Cl, Br, or I, the MM3 vibrational frequencies were compared with experimental vibrational frequencies. The rms error for vibrational

frequencies was 28 cm<sup>-1</sup> when compared with the 346 experimentally assigned vibrational frequencies for the fundamental modes of 12 acyl halides HCOF, HCOCl, HCOBr, CH<sub>3</sub>COF, CH<sub>3</sub>COCl, CH<sub>3</sub>COBr, CH<sub>3</sub>COI, *s-trans*- and *gauche*-CH<sub>3</sub>CH<sub>2</sub>COF, *s-trans*- and *gauche*-CH<sub>3</sub>CH<sub>2</sub>COCl, *s-trans*- and *gauche*-CH<sub>3</sub>CH<sub>2</sub>COBr, *gauche*- and *syn*-CH<sub>3</sub>CH(CH<sub>3</sub>)COF, and *gauche*- and *syn*-CH<sub>3</sub>CH(CH<sub>3</sub>)COCl. The rms error of the acyl halide frequencies was surprisingly smaller than that of hydrocarbons<sup>2</sup> (35 cm<sup>-1</sup>) and that of aldehydes and ketones<sup>3</sup> (42 cm<sup>-1</sup>).

## Results and Discussion

It was straightforward to assign the acyl halide vibrational frequencies generated by MM3<sup>4</sup> by

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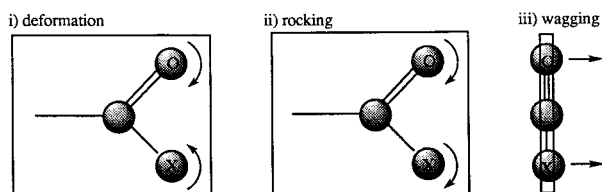
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normal vibrational mode analysis using the VIB-PLT program that graphically displays each fundamental vibrational mode. All the experimentally assigned fundamental vibrational frequencies were used in developing the parameters. The calculated vibrational frequencies for the fundamental vibrational modes of 12 acyl halides were compared with the values assigned from experimental studies and *ab initio* calculations<sup>5</sup> to establish the accuracy of the MM3 parameterization. The gas-phase vibrational spectra were preferred to liquid- or solid-phase spectra because the molecular mechanics calculations are based on isolated molecules. The rms deviations for acyl fluorides, chlorides, bromides, and an acyl iodide are 31  $\text{cm}^{-1}$ , 27  $\text{cm}^{-1}$ , 27  $\text{cm}^{-1}$ , and 13  $\text{cm}^{-1}$ , respectively.

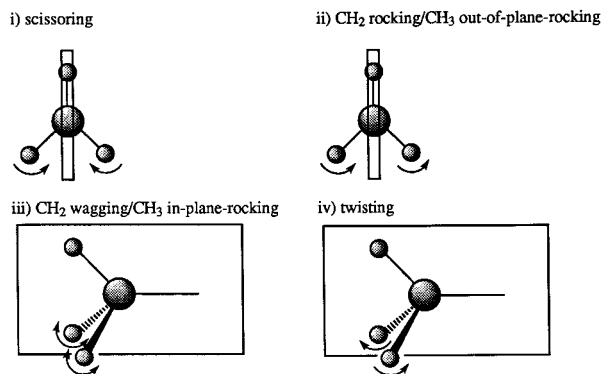
### VIBRATIONAL SPECTRA

The bending vibrational modes for the  $\text{O}=\text{C}-\text{X}$  moiety and the  $\text{CH}_2$  or  $\text{CH}_3$  moiety of acyl halides are depicted using the symmetry plane in Figure 1.

(a)  $-\text{C}(=\text{O})-\text{X}$  bending modes



(b)  $-\text{CH}_3$  or  $-\text{CH}_2$  bending modes



**FIGURE 1.** Definition of bending vibrational modes used for assigning vibrational spectra of acyl halides. Each mode is explained with the aid of the symmetry plane and arrows.

### FORMYL FLUORIDE, CHLORIDE, AND BROMIDE

Formyl halides have  $C_s$  symmetry with six fundamental vibrational modes, five  $A'$  modes and one  $A''$  mode. All of the experimental and calculated vibrational frequencies for these formyl halides are shown in Table I. The gas-phase IR spectrum of formyl fluoride<sup>6</sup> has been selected for comparison with our results. The experimental IR studies on formyl fluoride failed to find the out-of-plane  $\text{C}-\text{H}$  bending frequency of  $\text{HCOF}$ . The predicted value (1012  $\text{cm}^{-1}$ ) from the out-of-plane  $\text{C}-\text{H}$  bending frequency of  $\text{DCOF}$  (applying the Teller-Redlich product rule)<sup>6b,6c</sup> was essentially identical to our calculated value (1013  $\text{cm}^{-1}$ ). The rms deviation of our calculated frequencies for formyl fluoride compared with the experimental values<sup>6b</sup> was 23  $\text{cm}^{-1}$ .

Gas-phase IR study on formyl chloride has been reported previously.<sup>7</sup> Our calculated vibrational frequencies for formyl chloride were very similar to the experimental vibrational frequencies. The rms deviation from the experimental vibrational data<sup>7a</sup> was 18  $\text{cm}^{-1}$ .

Despite the lack of structural parameters for the very unstable formyl bromide, the gas-phase IR study on this compound has been reported recently by Yarwood et al.<sup>8</sup> They successfully assigned the vibrational frequencies for formyl bromide, with the exception of the  $\text{O}=\text{C}-\text{Br}$  in-plane bending frequency. Our calculated vibrational frequencies for formyl bromide (with predicted molecular structural parameters) was very close to the IR data of Yarwood et al. The rms deviation for formyl bromide was 19  $\text{cm}^{-1}$ .

In general, the vibrational frequencies of formyl halides were well predicted by our calculations with the exception of the  $\text{O}=\text{C}-\text{X}$  bending frequencies, which were calculated to have lower values than the corresponding experimental frequencies (see Table I). This appears to result from the electronegativity effects of the halides on the bending force constant parameter,  $k_b$ , for the  $\text{O}=\text{C}-\text{X}$  angles, which are not incorporated in the MM3 method. Compared with *ab initio* calculations, the MM3 calculations were as accurate as the scaled RHF/6-31G\* calculations with the advantage that only a fraction of the amount of computing time was required. In the case of formyl bromide, the RHF/3-21G\* calculations gave less satisfactory results than did MM3.

**TABLE I.**  
**Fundamental Vibrational Frequencies ( $\text{cm}^{-1}$ ) of Formyl Fluoride, Formyl Chloride, and Formyl Bromide.**

(a) Formyl fluoride (HCOF)						
Assignment	Symm.	IR (gas) <sup>a, b</sup>	IR (gas) <sup>c</sup>	<i>Ab initio</i> <sup>d, e</sup>	MM3	MM3 – IR <sup>a</sup>
C—H str	A'	2981	2976	3357 (3021)	2952	–29
C=O str	A'	1837	1834	2102 (1892)	1850	13
C—H bend	A'	1343	1344	1539 (1385)	1340	–3
C—F str	A'	1065	1064	1249 (1124)	1063	–2
C—H bend (o—p)	A''	(1012) <sup>f</sup>	—	1176 (1058)	1013	—
F—C=O bend	A'	663	661	738 (664)	622	–41
rms deviation						23 <sup>g</sup>

<sup>a</sup>Taken from ref. 6a.<sup>b</sup>Taken from ref. 6b.<sup>c</sup>Taken from ref. 6c.<sup>d</sup>Calculated at the RHF / 6-31G\* level, using the Gaussian-90 program, in this work.<sup>e</sup>The values in parentheses are those after applying a scaling factor of 0.9.<sup>f</sup>Obtained from the frequency ( $857 \text{ cm}^{-1}$ ) of the same vibrational mode of DCOF molecule using the Teller–Redlich product rule. For this vibrational mode a frequency of  $1000\text{--}1050 \text{ cm}^{-1}$  was predicted (ref. 6c), whereas the frequency of  $1175 \text{ cm}^{-1}$  was assumed from the study of ultraviolet spectrum [L. E. Giddings, Jr. and K. K. Innes, *J. Mol. Spectrosc.*, **6**, 528 (1961)].<sup>g</sup>The C—H out-of-plane bending frequency was not used in calculating the rms deviation.

(b) Formyl chloride (HCOCl)					
Assignment	Symm.	IR (gas) <sup>a</sup>	<i>Ab initio</i> <sup>b, c</sup>	MM3	MM3 – IR <sup>a</sup>
C—H str	A'	2929	3315 (2984)	2942	13
C=O str	A'	1784	2042 (1838)	1790	6
C—H bend	A'	1307	1493 (1344)	1300	–7
C—H bend (o—p)	A''	(932) <sup>d</sup>	1071 (964)	951	19
C—Cl str	A'	739	827 (744)	765	26
Cl—C=O bend	A'	458	511 (460)	432	–26
rms deviation					18 <sup>e</sup>

<sup>a</sup>Taken from ref. 7.<sup>b</sup>Calculated at the RHF / 6-31G\* level, using the Gaussian-90 program, in this work.<sup>c</sup>The values in parentheses are those after applying a scaling factor of 0.9.<sup>d</sup>D-L. Joo, D. J. Clouthier, and A. J. Merer, *J. Mol. Spectrosc.*, **174**, 353 (1995).<sup>e</sup>The C—H out-of-plane bending frequency was not used in calculating the rms deviation.

(c) Formyl bromide (HCOBr)					
Assignment	Symm.	IR (gas) <sup>a</sup>	<i>Ab initio</i> <sup>b, c</sup>	MM3	MM3 – IR <sup>a</sup>
C—H str	A'	2912	3289 (2960)	2925	13
C=O str	A'	1789	1912 (1721)	1783	–6
C—H bend	A'	1276	1477 (1329)	1281	5
C—H bend (o—p)	A''	893	1041 (937)	922	29
C—Br str	A'	646	712 (641)	674	28
Br—C=O bend	A'	(300) <sup>d</sup>	407 (366)	343	—
rms deviation					19 <sup>e</sup>

<sup>a</sup>Taken from ref. 8.<sup>b</sup>Calculated at the RHF / 3-21G\* level, using the Gaussian-94 program, in this work.<sup>c</sup>The values in parentheses are those after applying a scaling factor of 0.9.<sup>d</sup>Approximated value.<sup>e</sup>The Br—C=O bending frequency was not used in calculating the rms deviation.

## ACETYL HALIDES

The vibrational frequencies for the acetyl halides are shown in Table II. Acetyl halide has 15 fundamental vibrational modes, 10  $A'$  modes and 5  $A''$  modes. For acetyl fluoride, our calculated vibrational frequencies were compared with the gas-phase IR vibrational frequency data.<sup>9</sup> The unobserved frequency for the torsional vibrational mode was calculated<sup>9a</sup> to be  $123\text{ cm}^{-1}$  from the height of the torsional barrier ( $364\text{ cm}^{-1}$ ), as determined from the microwave spectrum of acetyl fluoride.<sup>10</sup> Our calculated vibrational frequency for the torsional mode was  $136\text{ cm}^{-1}$ , whereas a frequency of  $208\text{ cm}^{-1}$  for this mode was assigned from the liquid Raman spectrum.<sup>11</sup> The rms deviation of our calculations was  $37\text{ cm}^{-1}$ , compared with the experimental vibrational data by Berney et al.<sup>9a</sup>

For acetyl chloride, gas-phase IR spectroscopic studies have been reported.<sup>9b,12,13</sup> Two of these IR studies,<sup>9b,12</sup> showing almost identical assignments for the fundamental vibrational modes, determined both the asymmetric methyl deformation modes and asymmetric methyl stretching modes to be degenerate. MM3, however, agrees with a recent IR study by Durig et al.<sup>13</sup> who concluded these modes are not degenerate. The torsional frequency of  $238\text{ cm}^{-1}$  was reported previously from the Raman spectrum.<sup>11</sup> MM3 correctly gave  $148\text{ cm}^{-1}$ , which corresponds to the value from the recent IR study of  $163\text{ cm}^{-1}$ .<sup>13</sup> Our calculated vibrational frequencies for acetyl chloride had an rms deviation of  $24\text{ cm}^{-1}$ , compared with the experimental vibrational frequencies obtained by Durig et al.<sup>13</sup>

Our calculated vibrational frequencies of acetyl bromide were compared with the available gas-phase IR vibrational frequencies.<sup>9b</sup> It is of interest that MM3 indicated that the asymmetric methyl deformation modes were not degenerate. These modes were assigned to be degenerate by the experimental IR study. For acetyl bromide, our calculated vibrational frequencies had an rms deviation of  $26\text{ cm}^{-1}$ , compared with experimental IR data.<sup>9b</sup>

The vibrational frequencies of acetyl iodide also were calculated by the MM3 force field. Two experimental IR studies on acetyl iodide<sup>9b,14</sup> showed similar assignments for the fundamental vibrational frequencies with the exception of the out-of-plane methyl wagging mode. Our calculated vibrational frequencies for acetyl iodide had an

rms deviation of  $13\text{ cm}^{-1}$ , when compared with the gas-phase IR data of Ramsey and Ladd.<sup>9b</sup>

The main errors of the calculated acetyl halide vibrational frequencies resulted from the out-of-plane wagging mode (see Table II). It was shown that, for this vibrational mode, acetyl fluoride gave the largest error ( $88\text{ cm}^{-1}$ ) and acetyl iodide gave the smallest errors ( $15\text{ cm}^{-1}$ ). This again suggests that the bending force constant,  $k_b$ , for an angle directly connected to halogens, could be modified to reflect the electronegativity of the halogens to more accurately obtain the corresponding vibrational frequency.

## PROPIONYL FLUORIDE, CHLORIDE, AND BROMIDE

Propionyl halides exist as two stable conformers, *s-trans* and *gauche*. *s-trans*-Propionyl halides have  $C_s$  symmetry and 24 normal vibrational modes, 15  $A'$  modes and 9  $A''$  modes. The fundamental vibrational frequencies for *s-trans*-propionyl halides are presented in Table III. For *s-trans*-propionyl fluoride, two of the gas-phase IR vibrational frequencies<sup>15</sup> have been used for comparison. Our calculated vibrational frequency for the C—F stretching mode ( $1211\text{ cm}^{-1}$ ) was much higher than the IR experimental value ( $1119\text{ cm}^{-1}$ ). The value of the MM3 C—F stretching force parameter, which has been fixed to fit the overall vibrational frequencies for all of the acyl halide compounds, appears poor for reproducing the C—F stretching frequency for this particular compound. The rms deviation of our calculated vibrational frequencies for *s-trans*-propionyl fluoride was  $37\text{ cm}^{-1}$ , as compared with the gas-phase IR frequencies of Durig et al.<sup>15a</sup>

Our calculated vibrational frequencies of *s-trans*-propionyl chloride were compared with two gas-phase IR studies.<sup>15b,16</sup> It should be noted that our calculated vibrational frequencies were in agreement with the experimentally assigned vibrational frequencies, with the exception of a few H—C—H bending vibration modes. The rms deviation of our calculated frequencies for *s-trans*-propionyl chloride was  $26\text{ cm}^{-1}$  (compare with IR data of Durig et al.<sup>16</sup>).

The MM3 vibrational frequencies for *s-trans*-propionyl bromide were compared with the gas-phase IR vibrational frequencies reported by Frankiss et al.<sup>15b</sup> and Durig et al.<sup>17</sup> The calculated

**TABLE II.**  
**Fundamental Vibrational Frequencies ( $\text{cm}^{-1}$ ) of Acetyl Fluoride, Acetyl Chloride, Acetyl Bromide, and Acetyl Iodide.**

(a) Acetyl fluoride (CH <sub>3</sub> COF)						
Assignment	Symm.	IR (gas) <sup>a</sup>	IR (gas) <sup>b</sup>	<i>Ab initio</i> <sup>c, d</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A'	3043	3025	3350 (3015)	3049	6
CH <sub>3</sub> str(as)	A''	3004	3000	3298 (2968)	3019	15
CH <sub>3</sub> str(s)	A'	2955	2970	3233 (2910)	2931	–24
C=O str	A'	1870	1876	2121 (1909)	1882	12
CH <sub>3</sub> def(as)	A'	1440	1435	1618 (1450)	1429	–11
CH <sub>3</sub> def(as)	A''	1437	1435	1611 (1450)	1442	5
CH <sub>3</sub> def(s)	A'	1378	1379	1566 (1409)	1383	5
C—C str	A'	1188	1185	1368 (1231)	1240	52
CH <sub>3</sub> wag	A''	1054	1053	1187 (1068)	966	–88
CH <sub>3</sub> rock	A'	1000	1002	1122 (1010)	941	–59
C—F str	A'	826	832	937 (843)	785	–41
O=C—F sci	A'	598	598	655 (590)	627	29
O=C—F wag	A''	567	569	628 (565)	555	–12
O=C—F rock	A'	(420) <sup>e</sup>	473	441 (397)	450	—
Torsion	A''	(123) <sup>f</sup>	—	147 (132)	136	—
rms deviation						37 <sup>g</sup>

<sup>a</sup>Taken from ref. 9a, and assigned in consideration of the assignment of acetyl chloride and characteristic group frequencies.

<sup>b</sup>Taken from ref. 9b, and assigned in consideration of assignments for carbonyl fluoride, characteristic group frequencies, and the band contours of the CD<sub>3</sub>COF spectrum.

<sup>c</sup>Calculated at the RHF / 6-31G\* level, using the Gaussian-90 program, in this work.

<sup>d</sup>The values in parentheses are those after applying a scaling factor of 0.9.

<sup>e</sup>Calculated from the microwave data.

<sup>f</sup>Calculated from the torsional barrier (from MW).

<sup>g</sup>The O=C—F rocking and the torsional frequencies were not used in calculating the rms deviation.

(b) Acetyl chloride (CH <sub>3</sub> COCl)							
Assignment	Symm.	IR (gas) <sup>a</sup>	IR (gas) <sup>b</sup>	IR (gas) <sup>c</sup>	<i>Ab initio</i> <sup>d, e</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A'	3026	3020	3029	3338 (3004)	3045	19
CH <sub>3</sub> str(as)	A''	2993	3020	3029	3309 (2978)	3015	22
CH <sub>3</sub> str(s)	A'	2950	2945	2934 <sup>f</sup>	3234 (2911)	2928	–22
C=O str	A'	1821	1820	1822	2080 (1872)	1816	–5
CH <sub>3</sub> def(as)	A'	1417	1428	1432	1612 (1450)	1428	11
CH <sub>3</sub> def(as)	A''	1431	1428	1432	1606 (1445)	1449	18
CH <sub>3</sub> def(s)	A'	1366	1366	1370	1551 (1395)	1362	–4
C—C str	A'	1108	1106	1109	1228 (1105)	1111	3
CH <sub>3</sub> wag	A''	1028	1028	1029	1160 (1044)	958	–70
CH <sub>3</sub> rock	A'	958	958	958	1055 (960)	930	–28
C—Cl str	A'	607	605	608	665 (599)	627	20
O=C—Cl wag	A''	514	514	514	569 (512)	490	–24
O=C—Cl sci	A'	444	435	436 <sup>f</sup>	497 (447)	453	9
O=C—Cl rock	A'	357	346	348 <sup>f</sup>	370 (333)	360	3
Torsion	A''	163	—	238 <sup>f</sup>	152 (137)	148	–15
rms deviation							24

<sup>a</sup>Taken from ref. 13.<sup>b</sup>Taken from ref. 9b, and assigned in consideration of the characteristic group frequencies and band contours of the  $\text{CD}_3\text{COCl}$  spectrum.<sup>c</sup>Taken from ref. 12, and assigned in consideration of assignments for acetone and carbonyl chloride, characteristic group frequencies, and the band contours of the spectra of  $\text{CH}_2\text{DCOCl}$  and  $\text{CD}_3\text{COCl}$ .<sup>d</sup>Calculated at RHF / 6-31G\* level, using the Gaussian-90 program, in this work.<sup>e</sup>The values in parentheses are those after applying a scaling factor of 0.9.<sup>f</sup>From the liquid-phase Raman spectrum (ref. 11).

TABLE II.  
(Continued)

(c) Acetyl bromide (CH <sub>3</sub> COBr)						
Assignment	Symm.	IR (gas) <sup>a</sup>	Raman (liq.) <sup>b</sup>	<i>Ab initio</i> <sup>c, d</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A'	3029	3015	3312 (2981)	3015	– 14
CH <sub>3</sub> str(as)	A''	3017	2921	3293 (2964)	2986	– 31
CH <sub>3</sub> str(s)	A'	2945	2929	3223 (2901)	2899	– 46
C=O str	A'	1826	1812	1971 (1774)	1802	– 24
CH <sub>3</sub> def(as)	A'	1426	1418	1623 (1461)	1424	– 2
CH <sub>3</sub> def(as)	A''	1426	1418	1638 (1474)	1447	21
CH <sub>3</sub> def(s)	A'	1363	1352	1564 (1408)	1357	– 6
C—C str	A'	1089	1084	1221 (1099)	1080	– 9
CH <sub>3</sub> wag	A''	1005	988	1181 (1063)	953	– 52
CH <sub>3</sub> rock	A'	945	938	997 (897)	924	– 21
C—Br str	A'	563	555	604 (544)	579	16
O=C—Br wag	A''	490 <sup>d</sup>	—	560 (504)	465	– 25
O=C—Br sci	A'	335 <sup>d</sup>	338	394 (355)	362	27
O=C—Br rock	A'	305 <sup>d</sup>	304	328 (295)	301	– 4
Torsion	A''	—	—	178 (160)	148	—
rms deviation						26 <sup>f</sup>

<sup>a</sup>Taken from ref. 9b, and assigned in consideration of the assignments for acetyl chloride and characteristic group frequencies.  
<sup>b</sup>Taken from ref. 11.  
<sup>c</sup>Calculated at the RHF / 3-21G\* level, using the Gaussian-94 program, in this work.  
<sup>d</sup>The values in parentheses are those after applying a scaling factor of 0.9.  
<sup>e</sup>From the liquid-phase IR spectrum.  
<sup>f</sup>The torsional frequency was not used in calculating the rms deviation.

(d) Acetyl iodide (CH <sub>3</sub> COI)					
Assignment	Symm.	IR (gas) <sup>a</sup>	IR (gas) <sup>b</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A'	3016	3011	3036	20
CH <sub>3</sub> str(as)	A''	3016	3011	3008	– 8
CH <sub>3</sub> str(s)	A'	2940	2937	2920	– 20
C=O str	A'	1808	1817	1793	– 15
CH <sub>3</sub> def(as)	A'	1428	1421	1425	– 3
CH <sub>3</sub> def(as)	A''	1428	1429	1446	18
CH <sub>3</sub> def(s)	A'	1355	1353	1356	1
C—C str	A'	1075	1079	1059	– 16
CH <sub>3</sub> wag	A''	937 <sup>c</sup>	1074 <sup>d</sup>	952	15
CH <sub>3</sub> rock	A'	915	928	920	5
C—I str	A'	542	551	543	1
O=C—I wag	A''	476	462	454	– 22
O=C—I sci	A'	285 <sup>e</sup>	291	290	5
O=C—I rock	A'	264 <sup>e</sup>	271	267	3
Torsion	A''	—	134	139	—
rms deviation					13 <sup>f</sup>

<sup>a</sup>Taken from ref. 9(b), and assigned in consideration of the assignment of acetyl chloride and characteristic group frequencies.  
<sup>b</sup>Taken from ref. 14, and assigned in consideration of characteristic group frequencies and the band contours of the spectra of CH<sub>2</sub>DCOI, CHD<sub>2</sub>COI, and CD<sub>3</sub>COI.  
<sup>c</sup>Assigned as a Fermi resonance peak (ref. 14).  
<sup>d</sup>Assigned as a Fermi resonance peak (ref. 9b).  
<sup>e</sup>From the liquid-phase IR spectrum.  
<sup>f</sup>The torsional frequency was not used in calculating the rms deviation.

vibrational frequency for the C=O stretching mode ( $1800\text{ cm}^{-1}$ ) was close to the Frankiss results for this vibrational mode ( $1815\text{ cm}^{-1}$ ).<sup>15b</sup> Durig et al.'s assignment for the C=O stretching mode ( $1833\text{ cm}^{-1}$ ) was even higher than that of *s-trans*-propionyl chloride ( $1820\text{ cm}^{-1}$ ).<sup>16</sup> Our calculation for the out-of-plane CH<sub>3</sub> rocking vibrational mode ( $1024\text{ cm}^{-1}$ ) was close to Durig's assignment for this vibrational mode ( $1007\text{ cm}^{-1}$ ), which had been previously assigned too high by Frankiss et al.

( $1064\text{ cm}^{-1}$ ).<sup>15b</sup> Compared with the experimental vibrational frequencies assigned by Durig et al.,<sup>17</sup> the rms deviation of the MM3 frequencies for *s-trans*-propionyl bromide was  $30\text{ cm}^{-1}$ .

The vibrational frequency assignments for some of the C—H stretching modes for the *s-trans*-propionyl halides show significant differences between Frankiss's assignments<sup>15b</sup> and Durig's assignments,<sup>15a, 16, 17</sup> (see Table III), which may be attributed to the fact that the spectra were deter-

**TABLE III.**  
**Fundamental Vibrational Frequencies ( $\text{cm}^{-1}$ ) of *s-trans*-Propionyl Fluoride, *s-trans*-Propionyl Chloride, and *s-trans*-Propionyl Bromide.**

(a) <i>s-trans</i> -propionyl fluoride ( $\text{CH}_3\text{CH}_2\text{COF}$ )						
Assignment	Symm.	IR (gas) <sup>a, b</sup>	IR (gas) <sup>c</sup>	<i>Ab initio</i> <sup>d, e</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A'	3000	2964 <sup>g</sup>	3303 (2973)	2986	–14
CH <sub>3</sub> str(as)	A''	2997 <sup>f</sup>	3001	3293 (2964)	2988	–9
CH <sub>2</sub> str(as)	A''	2969	2940 <sup>g</sup>	3256 (2930)	2971	2
CH <sub>2</sub> str(s)	A'	2961	2939	3227 (2904)	2921	–40
CH <sub>3</sub> str(s)	A'	2942	2935	3223 (2901)	2892	–50
C=O str	A'	1864	1862	2114 (1903)	1879	15
CH <sub>3</sub> def(as)	A'	1474	1475	1645 (1481)	1456	–18
CH <sub>3</sub> def(as)	A''	1463	1464	1639 (1475)	1464	1
CH <sub>2</sub> def	A'	1428	1429	1611 (1450)	1429	1
CH <sub>3</sub> def(s)	A'	1402	1390	1578 (1420)	1477	75
CH <sub>2</sub> wag	A'	1359	1360	1539 (1385)	1383	24
CH <sub>2</sub> twist	A''	1266	1266	1406 (1265)	1215	–51
C—F str	A'	1119	1119	1291 (1162)	1211	92
CH <sub>3</sub> rock(out)	A''	1097	1097	1228 (1105)	1028	–69
CH <sub>3</sub> rock(in)	A'	1075	1075	1196 (1076)	1028	–47
C—C str(as)	A'	999	999	1083 (975)	987	–12
C—C str(s)	A'	818	814	885 (797)	804	–14
CH <sub>2</sub> rock	A''	802	813 <sup>g</sup>	906 (815)	836	34
O=C—F def	A'	623	615	680 (612)	599	–24
O=C—F wag	A''	534 <sup>g</sup>	547	595 (536)	553	19
C—C—C bend	A'	460	459	497 (447)	462	2
O=C—F rock	A'	251	249	263 (237)	274	23
CH <sub>3</sub> torsion	A''	204	194 <sup>h</sup>	234 (211)	225	21
Torsion(as)	A''	82	85 <sup>i</sup>	87 (78)	82	0
rms deviation						37

<sup>a</sup>Taken from ref. 15a.

<sup>b</sup>Assigned in consideration of assignment for propionyl chloride (ref. 16), and the characteristic group frequencies.

<sup>c</sup>Taken from ref. 15b.

<sup>d</sup>Calculated at the RHF/6-31G\* level, using the Gaussian-92 program, in this work.

<sup>e</sup>The values in parentheses are those after applying a scaling factor of 0.9.

<sup>f</sup>Assigned from the liquid-phase Raman spectrum.

<sup>g</sup>Assigned from the solid-phase IR spectrum.

<sup>h</sup>Calculated from the microwave data. The frequency of  $205\text{ cm}^{-1}$  was assigned from the liquid-phase IR spectrum, whereas the frequency of  $227\text{ cm}^{-1}$  was assigned from the solid-phase IR spectrum.

<sup>i</sup>Calculated from the microwave data. The frequency of  $105\text{ cm}^{-1}$  was assigned from the liquid-phase IR spectrum, and the frequency of  $143\text{ cm}^{-1}$  was assigned from the solid-phase IR spectrum.

TABLE III.  
(Continued)

(b) <i>s-trans</i> -propionyl chloride (CH <sub>3</sub> CH <sub>2</sub> COCl)						
Assignment	Symm.	IR (gas) <sup>a,b</sup>	IR (gas) <sup>c</sup>	<i>Ab initio</i> <sup>d,e</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A''	3001 <sup>f</sup>	2999	3306 (2975)	2988	–3
CH <sub>3</sub> str(as)	A'	2999	2981 <sup>h</sup>	3294 (2965)	2987	–12
CH <sub>2</sub> str(s)	A'	2958	2936	3267 (2940)	2918	–40
CH <sub>3</sub> str(s)	A'	2935	2930	3233 (2910)	2892	–43
CH <sub>2</sub> str(as)	A''	2994 <sup>g</sup>	2930 <sup>h</sup>	3226 (2903)	2967	–27
C=O str	A'	1820	1830	2072 (1865)	1813	–7
CH <sub>3</sub> def(as)	A'	1468	1472	1643 (1479)	1455	–13
CH <sub>3</sub> def(as)	A''	1456	1456	1639 (1475)	1464	8
CH <sub>2</sub> def	A'	1436	1421	1606 (1445)	1422	–14
CH <sub>3</sub> def(s)	A'	1420	1385	1572 (1415)	1465	45
CH <sub>2</sub> wag	A'	1340	1339	1515 (1364)	1378	38
CH <sub>2</sub> twist	A''	1260	1261	1405 (1265)	1221	–39
CH <sub>3</sub> rock(out)	A''	1803 <sup>f</sup> (1018) <sup>i</sup>	1088	1210 (1089)	1025	–58
CH <sub>3</sub> rock(in)	A'	1088	1084	1201 (1081)	1082	–6
C—C str(as)	A'	1018 (987) <sup>i</sup>	1016	1104 (994)	1021	3
C—C str(s)	A'	926	926	1010 (909)	949	23
CH <sub>2</sub> rock	A''	788	788	867 (780)	826	38
C—Cl str	A'	698	697	758 (682)	691	–7
O=C—Cl wag	A''	496	505	547 (492)	494	–2
O=C—Cl def(s)	A'	441	441	497 (447)	439	–2
C—C—C bend	A'	356	359	390 (351)	359	3
O=C—Cl rock	A'	224	229	247 (222)	252	28
CH <sub>3</sub> torsion	A''	204	196 <sup>j</sup>	239 (215)	225	21
Torsion(as)	A''	79	71 <sup>k</sup>	84 (76)	76	–3
rms deviation						26

<sup>a</sup>Taken from ref. 16.  
<sup>b</sup>Assigned in consideration of assignment for haloacetyl halides and the characteristic group frequencies.  
<sup>c</sup>Taken from ref. 15b.  
<sup>d</sup>Calculated at the RHF / 6-31G\* level, using the Gaussian-92 program, in this work.  
<sup>e</sup>The values in parentheses are those after applying a scaling factor of 0.9.  
<sup>f</sup>Assigned from the solid-phase Raman spectrum.  
<sup>g</sup>Assigned from the liquid-phase Raman spectrum.  
<sup>h</sup>Assigned from the solid-phase IR spectrum.  
<sup>i</sup>Reassigned to be 1018 cm<sup>–1</sup> for the CH<sub>3</sub> out-of-plane rocking mode and later 987 cm<sup>–1</sup> for the C—C—C antisymmetric stretching mode (ref. 17).  
<sup>j</sup>Derived from combination tone in the gas phase IR spectrum. The frequency of 205 cm<sup>–1</sup> was assigned from the liquid-phase IR spectrum, whereas the frequency of 214 cm<sup>–1</sup> was assigned from the solid-phase IR spectrum.  
<sup>k</sup>Derived from combination tone in the gas-phase IR spectrum.

mined in different states. Overall, our calculations for the C—H stretching frequencies showed much lower values than the corresponding values determined from the experimental IR studies.<sup>15–17</sup> These lower frequencies obtained by our calculations appear to be from the insufficient correction of force constants for C—H bonds in the  $\beta$ - and  $\gamma$ -posi-

tions relative to the electronegative halogens. The MM3 twist and rocking frequencies showed lower values than either Durig's or Frankiss's assignments for these modes, as shown for acetyl halides (see Table II).

For vibrational frequencies of the higher energy *gauche*-propionyl halides, our calculated frequen-



**TABLE III.**  
(Continued)(c) *s-trans*-propionyl bromide (CH<sub>3</sub>CH<sub>2</sub>COBr)

Assignment	Symm.	IR (gas) <sup>a,b</sup>	IR (gas) <sup>c</sup>	<i>Ab initio</i> <sup>d,e</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A''	3004 <sup>f</sup>	2999	3294 (2965)	2988	– 16
CH <sub>3</sub> str(as)	A'	2999	2992 <sup>f</sup>	3284 (2956)	2987	– 12
CH <sub>2</sub> str(s)	A'	2956	2927	3233 (2908)	2898	– 57
CH <sub>2</sub> str(as)	A''	2991 <sup>g</sup>	2954	3266 (2939)	2937	– 54
CH <sub>3</sub> str(s)	A'	2938	2930	3220 (2898)	2882	– 56
C=O str	A'	1833	1815	1968 (1771)	1800	– 33
CH <sub>3</sub> def(as)	A'	1467	1472	1667 (1500)	1454	– 13
CH <sub>3</sub> def(as)	A''	1450	1463	1668 (1501)	1464	14
CH <sub>2</sub> def	A'	1436	1418	1613 (1452)	1417	– 19
CH <sub>3</sub> def(s)	A'	1417	1386	1588 (1429)	1461	44
CH <sub>2</sub> wag	A'	1333	1334	1491 (1342)	1376	43
CH <sub>2</sub> twist	A''	1257	1258	1423 (1281)	1220	– 37
CH <sub>3</sub> rock(out)	A''	1007	1064	1228 (1105)	1024	17
CH <sub>3</sub> rock(in)	A'	1085	1081	1204 (1084)	1061	– 24
C—C str(as)	A'	986	1009	1070 (963)	1018	32
C—C str(s)	A'	901	897	953 (858)	928	27
CH <sub>2</sub> rock	A''	784	782	879 (791)	821	37
C—Br str	A'	682	681	743 (669)	659	– 23
O=C—Br wag	A''	464	476	540 (486)	473	9
O=C—Br def	A'	359	358	404 (364)	353	– 6
C—C—C bend	A'	299	296	339 (305)	311	12
O=C—Br rock	A'	209	206	227 (204)	225	16
CH <sub>3</sub> torsion	A''	202	199 <sup>h</sup>	217 (195)	224	22
Torsion(as)	A''	76	66 <sup>h</sup>	88 (79)	79	3
rms deviation						30

<sup>a</sup>Taken from ref. 17.<sup>b</sup>Assigned in consideration of assignment for propionyl fluoride (ref. 15a), propionyl chloride (ref. 16), and the characteristic group frequencies.<sup>c</sup>Taken from ref. 15b.<sup>d</sup>Calculated at the RHF / 3-21G\* level, using the Gaussian-94 program, in this work.<sup>e</sup>The values in parentheses are those after applying a scaling factor of 0.9.<sup>f</sup>From the solid-phase IR spectrum.<sup>g</sup>From the liquid-phase Raman spectrum.<sup>h</sup>Derived from the combination tone in the gas-phase IR spectrum.

cies were compared with those determined in the gas phase by Durig et al.<sup>15a,16,17</sup> and Frankiss et al.<sup>15b</sup> The fundamental frequencies for *gauche*-propionyl halides are shown in Table IV. Whereas with MM3 it is straightforward to calculate vibrational frequencies for higher energy conformers, experimentally high-resolution instruments and additional work are required; for example, annealing experiments are essentially required for correctly assigning vibrational frequencies for higher energy conformers.

Durig et al.<sup>15a</sup> assigned almost identical vibrational frequencies for the C—H stretching modes and H—C—H bending modes of *gauche*-propionyl fluoride as those assigned to the *s-trans* conformation. MM3 predicted somewhat different vibrational frequencies for some of these modes. For example, the antisymmetric CH<sub>2</sub> stretching and CH<sub>2</sub> twist modes the *gauche* frequencies were 2932 cm<sup>–1</sup> and 1271 cm<sup>–1</sup>, respectively. From the *s-trans* conformations, 2921 cm<sup>–1</sup> and 1215 cm<sup>–1</sup> were calculated, respectively. For the CH<sub>3</sub> rocking

**TABLE IV.**  
**Fundamental Vibrational Frequencies (cm<sup>-1</sup>) of *gauche*-Propionyl Fluoride, *gauche*-Propionyl Chloride, and *gauche*-Propionyl Bromide.**

(a) <i>gauche</i> -propionyl fluoride (CH <sub>3</sub> CH <sub>2</sub> COF)					
Assignment	Symm.	IR (gas) <sup>a</sup>	<i>Ab initio</i> <sup>a, b</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A	3000	3281 (2953)	2987	– 13
CH <sub>3</sub> str(as)	A	2997 <sup>c</sup>	3300 (2970)	2989	– 8
CH <sub>2</sub> str(as)	A	2960	3321 (2989)	2998	38
CH <sub>2</sub> str(s)	A	2961	3229 (2906)	2932	– 29
CH <sub>3</sub> str(s)	A	2942	3220 (2898)	2894	– 48
C=O str	A	1864	2043 (1839)	1884	20
CH <sub>3</sub> def(as)	A	1474	1678 (1510)	1457	– 17
CH <sub>3</sub> def(as)	A	1463	1671 (1504)	1464	1
CH <sub>2</sub> def	A	1443	1635 (1472)	1436	– 7
CH <sub>3</sub> def(s)	A	1402	1584 (1426)	1452	50
CH <sub>2</sub> wag	A	1366	1488 (1339)	1375	9
CH <sub>2</sub> twist	A	1266	1443 (1299)	1271	5
C—F str	A	1178	1332 (1199)	1183	5
CH <sub>3</sub> rock(in)	A	1090 <sup>d</sup>	1236 (1112)	1026	– 64
CH <sub>3</sub> rock(out)	A	1030	1174 (1057)	1018	– 12
C—C str(as)	A	965	1026 (923)	973	8
C—C str(s)	A	792 <sup>d</sup>	868 (781)	750	– 42
CH <sub>2</sub> rock	A	802	898 (808)	835	33
O=C—F def	A	567	614 (553)	578	11
O=C—F wag	A	698	751 (676)	673	25
C—C—C bend	A	356 <sup>c</sup>	283 (255)	282	– 74
O=C—F rock	A	448	458 (412)	436	– 12
CH <sub>3</sub> torsion	A	172	242 (218)	209	37
Torsion(as)	A	54	76 (68)	58	4
rms deviation					31

<sup>a</sup>Taken from ref. 15a.  
<sup>b</sup>The values in parentheses are those after applying a scaling factor of 0.9.  
<sup>c</sup>Assigned from the liquid-phase Raman spectrum.  
<sup>d</sup>Assigned from the gas-phase Raman spectrum.

modes MM3 gave lower vibrational frequencies. It was not easy to assign each mode to a single vibration, because there is considerable mixing among C—F stretching and bending modes below 1000 cm<sup>-1</sup>. From the energy distribution matrices of *gauche*-propionyl fluoride, it was found that O=C—F deformation and O=C—F wagging modes of *gauche*-propionyl fluoride were highly mixed. The rms error of our calculated vibrational frequencies was 31 cm<sup>-1</sup>, from Durig’s observed values.<sup>15a</sup>

For *gauche*-propionyl chloride, the calculated vibrational frequencies were in agreement with the

gas-phase IR data,<sup>16</sup> except for a few bending modes, including CH<sub>2</sub> wagging, CH<sub>2</sub> twisting, and CH<sub>3</sub> out-of-plane rocking modes. The rms error of the calculated vibrational frequencies was 27 cm<sup>-1</sup>, from Durig’s values.<sup>16</sup>

MM3 also reproduced the vibrational frequencies for *gauche*-propionyl bromide fairly well. For the CH<sub>2</sub> stretching, CH<sub>2</sub> wagging, and CH<sub>2</sub> twisting modes, MM3 showed relatively large differences from the gas-phase IR values.<sup>17</sup> The rms error of the calculated vibrational frequencies for *gauche*-propionyl bromide was 33 cm<sup>-1</sup>, based on Durig’s experimental values.<sup>17</sup>

**TABLE IV.**  
(Continued)(b) *gauche*-propionyl chloride ( $\text{CH}_3\text{CH}_2\text{COCl}$ )

Assignment	Symm.	IR (gas) <sup>a</sup>	<i>Ab initio</i> <sup>b,c</sup>	MM3	MM3 – IR <sup>a</sup>
$\text{CH}_3$ str(as)	A	3001 <sup>d</sup>	3311 (2980)	2995	–6
$\text{CH}_3$ str(as)	A	2999	3290 (2961)	2990	–9
$\text{CH}_2$ str(s)	A	2958	3248 (2923)	2940	–18
$\text{CH}_3$ str(s)	A	2939 <sup>e</sup>	3218 (2896)	2896	–43
$\text{CH}_2$ str(as)	A	2994 <sup>f</sup>	3280 (2952)	2988	–6
$\text{C}=\text{O}$ str	A	1820	1971 (1774)	1816	–4
$\text{CH}_3$ def(as)	A	1472	1674 (1507)	1459	–13
$\text{CH}_3$ def(as)	A	1456	1669 (1502)	1463	7
$\text{CH}_2$ def	A	1448	1635 (1472)	1440	–8
$\text{CH}_3$ def(s)	A	1400	1582 (1424)	1451	51
$\text{CH}_2$ wag	A	1312 <sup>f</sup>	1474 (1327)	1368	56
$\text{CH}_2$ twist	A	1260	1424 (1282)	1204	–56
$\text{CH}_3$ rock	A	1129	1259 (1133)	1110	–19
$\text{CH}_3$ rock	A	1072 <sup>f</sup>	1208 (1087)	1023	–49
$\text{C}—\text{C}$ str(as)	A	982	1051 (946)	1005	23
$\text{C}—\text{C}$ str(s)	A	910	954 (859)	944	34
$\text{CH}_2$ rock	A	805 <sup>f</sup>	893 (804)	823	18
$\text{C}—\text{Cl}$ str	A	575	582 (524)	568	–7
$\text{O}=\text{C}—\text{Cl}$ wag	A	636	718 (646)	628	–8
$\text{O}=\text{C}—\text{Cl}$ def(s)	A	434	457 (411)	455	21
$\text{C}—\text{C}—\text{C}$ bend	A	235	250 (225)	256	21
$\text{O}=\text{C}—\text{Cl}$ rock	A	376	409 (368)	360	–16
$\text{CH}_3$ torsion	A	202	232 (209)	198	–4
Torsion(as)	A	65	80 (72)	64	–1
rms deviation					27

<sup>a</sup>Taken from ref. 16.<sup>b</sup>Calculated at the RHF / 6-31G\* level, using the Gaussian-90 program, in this work.<sup>c</sup>The values in parentheses are those after applying a scaling factor of 0.9.<sup>d</sup>Assigned from the solid-phase Raman spectrum.<sup>e</sup>Assigned from the gas-phase Raman spectrum.<sup>f</sup>Assigned from the liquid-phase Raman spectrum.**CARBONYL STRETCHING VIBRATIONAL FREQUENCIES**

The characteristically intense  $\text{C}=\text{O}$  stretching vibrational frequencies for acyl halides were well reproduced by our molecular mechanics calculations, which showed a reasonable trend of decreasing vibrational frequencies due to the decreasing electronegativity of halogens from acetyl fluoride to acetyl iodide. Allinger et al.<sup>3a</sup> demonstrated that the  $\text{C}=\text{O}$  stretching frequencies for cyclic ketones

were changed mainly as the degree of coupling varied with the adjacent  $\text{C}—\text{C}$  stretching vibrations. We calculated the  $\text{C}=\text{O}$  stretching frequencies for various geometries of acyl halides (Table V), and found that the  $\text{C}=\text{O}$  stretching frequencies for acyl halides were varied proportionally with the changes of  $\angle(\text{O}=\text{C}—\text{X})$  as represented in Figure 2. The change in the  $\text{C}=\text{O}$  stretching frequencies for acyl bromides were much more sensitive to this angle than were the acyl

TABLE IV.  
(Continued)

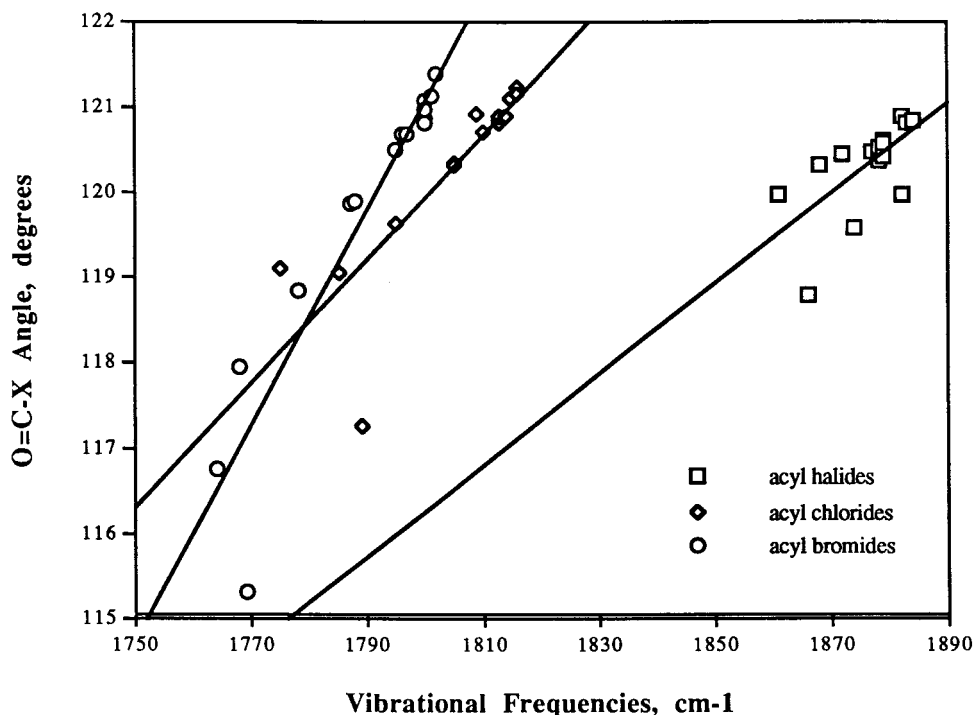
(c) <i>gauche</i> -propionyl bromide (CH <sub>3</sub> CH <sub>2</sub> COBr)					
Assignment	Symm.	IR (gas) <sup>a</sup>	<i>Ab initio</i> <sup>b, c</sup>	MM3	MM3 – IR <sup>a</sup>
CH <sub>3</sub> str(as)	A	3004 <sup>d</sup>	3294 (2965)	2994	– 10
CH <sub>3</sub> str(as)	A	2999	3279 (2951)	2988	– 11
CH <sub>2</sub> str(s)	A	2951 <sup>e</sup>	3246 (2921)	2894	– 57
CH <sub>2</sub> str(as)	A	2991 <sup>f</sup>	3311 (2980)	2962	– 29
CH <sub>3</sub> str(s)	A	2938	3218 (2896)	2910	– 28
C=O str	A	1833	1965 (1769)	1801	– 32
CH <sub>3</sub> def(as)	A	1474	1675 (1508)	1458	– 16
CH <sub>3</sub> def(as)	A	1450	1668 (1501)	1468	18
CH <sub>2</sub> def	A	1436	1633 (1470)	1438	2
CH <sub>3</sub> def(s)	A	1398	1579 (1421)	1450	52
CH <sub>2</sub> wag	A	1306 <sup>f</sup>	1471 (1324)	1370	64
CH <sub>2</sub> twist	A	1249	1422 (1280)	1202	– 47
CH <sub>3</sub> rock	A	1119	1258 (1132)	1093	– 26
CH <sub>3</sub> rock	A	1080 <sup>f</sup>	1204 (1084)	1021	– 59
C—C str(as)	A	978	1047 (942)	1002	24
C—C str(s)	A	901	953 (858)	932	31
CH <sub>2</sub> rock	A	808 <sup>e</sup>	892 (803)	816	8
C—Br str	A	548	582 (524)	538	– 10
O=C—Br wag	A	626	699 (629)	586	– 40
O=C—Br def(s)	A	354	399 (359)	382	28
C—C—C bend	A	327	370 (333)	308	– 19
O=C—Br rock	A	224	239 (215)	196	– 28
CH <sub>3</sub> torsion	A	—	225 (203)	234	—
Torsion(as)	A	71	84 (76)	72	1
4rms deviation					33 <sup>g</sup>

<sup>a</sup>Taken from ref. 17.  
<sup>b</sup>Calculated at the RHF / 3-21G\* level, using the Gaussian-94 program, in this work.  
<sup>c</sup>The values in parentheses are those after applying an 0.9 scaling factor.  
<sup>d</sup>Assigned from the solid-phase IR spectrum.  
<sup>e</sup>Assigned from the gas-phase Raman spectrum.  
<sup>f</sup>Assigned from the liquid-phase Raman spectrum.  
<sup>g</sup>The CH<sub>3</sub> bond torsional frequency was not used in calculating the rms deviation.

**TABLE V.** Carbonyl Stretching Frequencies (in  $\text{cm}^{-1}$ ) and Angles  $\angle(\text{O}=\text{C}-\text{X})$  (in Degrees) of Acyl Halide Compounds.

	X = F		X = Cl		X = Br	
	Exp.	MM3	Exp.	MM3	Exp.	MM3
$\text{CH}_3\text{COX}$	1870 <sup>a</sup>	1882	1820 <sup>b</sup>	1816	1826 <sup>b</sup>	1802
$\angle(\text{O}=\text{C}-\text{X})$		(120.882)		(121.235)		(121.380)
$\text{CH}_3\text{CH}_2\text{COX}$ , <i>s-trans</i>	1864 <sup>c</sup>	1879	1820 <sup>d</sup>	1813	1833 <sup>e</sup>	1860
$\angle(\text{O}=\text{C}-\text{X})$		(120.609)		(120.847)		(120.860)
$\text{CH}_3\text{CH}_2\text{COX}$ , <i>gauche</i>	1864 <sup>c</sup>	1884	1820 <sup>d</sup>	1816	1833 <sup>e</sup>	1801
$\angle(\text{O}=\text{C}-\text{X})$		(120.833)		(121.146)		(121.130)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COX}$		1879	1801 <sup>f</sup>	1813	1810 <sup>f</sup>	1800
$\angle(\text{C}=\text{C}-\text{X})$		(120.584)		(120.814)		(120.816)
$(\text{CH}_3)_2\text{CHCOX}$ , <i>gauche</i>	1856 <sup>g</sup>	1878	1810 <sup>h</sup>	1810		1795
$\angle(\text{O}=\text{C}-\text{X})$		(120.518)		(120.694)		(120.486)
$(\text{CH}_3)_2\text{CHCOX}$ , <i>syn</i>	1856 <sup>g</sup>	1883	1810 <sup>h</sup>	1814		1797
$\angle(\text{O}=\text{C}-\text{X})$		(120.799)		(120.887)		(120.684)
$(\text{CH}_3)_3\text{CCOX}$		1877		1805		1788
$\angle(\text{O}=\text{C}-\text{X})$		(120.459)		(120.330)		(119.894)
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COX}$		1878		1813		1796
$\angle(\text{O}=\text{C}-\text{X})$		(120.372)		(120.888)		(120.665)
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{COX}$		1872		1805		1787
$\angle(\text{O}=\text{C}-\text{X})$		(120.431)		(120.318)		(119.873)
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{COX}$		1879	1795 <sup>i</sup>	1815		1800
$\angle(\text{O}=\text{C}-\text{X})$		(120.419)		(121.099)		(121.084)
$(\text{CH}_3)_3\text{CCH}_2\text{COX}$		1882		1809		1800
$\angle(\text{O}=\text{C}-\text{X})$		(119.968)		(120.915)		(120.963)
$\text{CH}_3\text{C}(\text{CH}(\text{CH}_3)_2)_2\text{COX}$		1868		1795		1778
$\angle(\text{O}=\text{C}-\text{X})$		(120.306)		(119.624)		(118.838)
$\text{CH}_3\text{C}(\text{tert-Bu})_2\text{COX}$		1861		1785		1768
$\angle(\text{O}=\text{C}-\text{X})$		(119.959)		(119.045)		(117.940)
$(\text{CH}(\text{CH}_3)_2)_3\text{CCOX}$		1874		1775		1764
$\angle(\text{O}=\text{C}-\text{X})$		(119.564)		(119.107)		(116.744)
$(\text{tert-Bu})_3\text{CCOX}$		1866		1789		1769
$\angle(\text{O}=\text{C}-\text{X})$		(118.781)		(117.244)		(115.311)

<sup>a</sup>Taken from ref. 9a.<sup>b</sup>Taken from ref. 9b.<sup>c</sup>Taken from ref. 15a.<sup>d</sup>Taken from ref. 16.<sup>e</sup>Taken from ref. 17.<sup>f</sup>From the liquid-phase IR spectrum [J. Som, et al., *Ind. J. Pure Appl. Phys.*, **12**, 149 (1974)].<sup>g</sup>Taken from ref. 18.<sup>h</sup>From the liquid-phase Raman spectrum (ref. 19).<sup>i</sup>From the liquid-phase IR spectrum [R. Das, et al., *Ind. J. Pure Appl. Phys.*, **17**, 390 (1979)].



**FIGURE 2.** Correlations between the carbonyl stretching vibrational frequencies ( $\text{cm}^{-1}$ ) and  $\text{O}=\text{C}-\text{X}$  angles (degrees), where X is F, Cl, or Br, for acyl halides according to MM3.

chlorides and fluorides. Some of the highly crowded compounds, such as tri-*tert*-butylacetyl chloride and tri-*tert*-butylacetyl bromide, showed deviations from the proportionality.

## Conclusion

Use of the newly developed MM3 acyl halide force field showed good overall agreement with the experimental vibrational spectra. It was also shown that vibrational spectra for some acyl halides not yet studied experimentally have been predicted by molecular mechanics calculations.

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